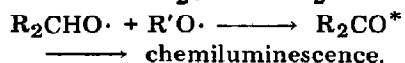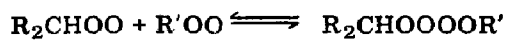xidation processes [2, 3] arises from a relatively efficient production of excited states from alkoxy radical disproportionations. Such alkoxy radicals can arise in low concentrations from non-Russell termination pathways of dialkyl tetroxides:

$$R_2CHOO + R'OO \rightleftharpoons R_2CHOOOOR'$$

$$\xrightarrow{\text{major}} R_2CO + O_2 + R'OH$$
$$\xrightarrow{\text{minor}} R_2CHO\cdot + O_2 + R'O\cdot$$
$$R_2CHO\cdot + R'O\cdot \longrightarrow R_2CO^*$$
$$\longrightarrow \text{chemiluminescence.}$$

1 S. K. Ho and J. B. DeSousa, J. Chem. Soc., 1788 (1961).
2 R. F. Vasil'ev, Progress in Reaction Kinetics, 4 (1967) 305 and references therein.
3 G. Lundeen and R. L. Livingston, Photochem. Photobiol., 4 (1965) 1085.

δ8

Major Emitting Species in Phosphorus Chemiluminescence

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The phosphorescence of phosphorus oxidation is the oldest and the best known chemiluminescing reaction, but a definitive spectroscopic study of this classic system has been lacking. In this talk we report the results of an investigation of the oxidation of P_4 vapor under atmospheric conditions, with added H_2O or D_2O vapor. The visible and ultraviolet spectrum of the reaction consists of discrete band structure in the 228.8 - 272.1 nm region and a broad continuum onsetting at 335 nm and extending to 800 nm and longer, upon which are superimposed a number of weak bands from 450 - 650 nm. Discrete band emissions at 228.8 - 272.1 nm belong to the PO γ-system transitions, $PO(A^2\Sigma^+) \rightarrow PO(X^2\Pi)$. Spectral changes arising from the substitution of D_2O vapor for H_2O vapor in the reaction led to the assignment of the weak bands at 450 - 650 nm to HPO (or DPO), $\tilde{A}(^1A'') \rightarrow \tilde{X}(^1A)$. The main band emission in the visible region, the broad continuum which cannot be identified with any simple electronic transition, exhibits the kinetic and spectral characteristics of an excimer.

In this case the excimer is $(PO^*...PO)$ and the equilibrium reaction for its formation is $(PO^*...PO) \rightleftharpoons PO(^4\Pi) + PO(B^2\Pi \rightleftharpoons PO(B^2\Sigma^+_*) + PO(X^2\Pi)$. The existence of the $(PO)^*_2$ excimer has been confirmed by affecting the dynamic of this equilibrium through dilution with nitrogen gas and through thermal dissociation of the excimer, resulting in the appearance of the formerly quenched (0,0) transition of the PO β-emission in the spectrum. Our investigation has eliminated the possibility that the visible continuum arises from either PO_2 or HOPO. Enough information has been extracted from temperature dependent studies to construct the approximate shapes of the potential energy surfaces of the ground ($\Delta\bar{\nu}_g = 35 \pm 200$ cm^{-1}) and the first excited states ($\Delta\bar{\nu}_{ex} = 846 \pm 200$ cm^{-1}) of the $(PO)^*_2$ excimer.

δ10

The Quantum Yield of Fluorescence of Quinine Bisulphate, Azulene and 9,10-Diphenylanthracene

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The quantum yield of fluorescence of quinine bisulphate (in $1N$ H_2SO_4) has been determined by an absolute method involving the rise in temperature of a solution due to light energy absorbed but not emitted as luminescence. Quinine bisulphate (in 1 N H_2SO_4) and potassium chromate (in 0.05 M KOH) were compared. A measured quantity of electrical energy (E_q and E_K, respectively) was put into the systems so that the heating (and cooling) curves were made to coincide. A 366 nm interference filter (100 A band pass and blocking to infinity) was utilized in connection with a 500 W high-pressure mercury arc. Temperature changes were monitored with a potted glass-bead thermistor in conjunction with a Jones impedance bridge, operating in the A.C. mode, and a lock-in amplifier at 4000 Hz (100 μV sensitivity and 300 ms time constant). At 25.00 °C the temperature coefficient was 760 Ω deg^{-1} while solution temperature fluctuations were about 0.10 Ω, and total changes over a 500 s experiment were about 100 Ω.